Art. XVI.—*On the Spectra of the Alkalies.*

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(Communicated by R. L. J. Ellery, C.M.G., F.R.S.)

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In the paper I venture to lay before the Royal Society of Victoria, I have attempted to determine the values of the wave lengths of the spectrum lines of the alkalies, as formed into series by Kaiser and Runge, by means of a new formula. To this formula I have given the shape $\lambda^n = x + \frac{y}{n^2 - z}$, λ meaning the wave length, n a whole number, commencing with 2, and x, y, z 3 constants. It requires three equations to determine these constants. Supposing three members of a series, viz., a, b, c, are known to form the series 3, 4, 5, then we get the three equations:

$$a = x + \frac{y}{9 - z}$$

$$b = x + \frac{y}{16 - z}$$

$$c = x + \frac{y}{25 - z}$$

which give the solution:

$$z = 9 - \frac{112(b - c)}{16(a - b) - 7(a - c)}$$

$$y = \frac{(a - b)(9 - z)(16 - z)}{7}$$

$$x = a - \frac{y}{9 - z}$$

If the numerals are respectively 4, 5, 6, the values are:

$$z = \frac{180(b - c)}{20(a - b) - 9(a - c)}$$

$$y = \frac{(a - b)(16 - z)(25 - z)}{9}$$

$$x = a - \frac{y}{16 - z}$$

Different combinations of numerals will of course require different values for a solution, but these are easily determined by deducting their square numbers and multiplying the differences respectively.

I shall refer to the three constants by calling x the root, because it is identical in value to Balmer's constant; y the amplitude, because its square root gives the final number of the series; and z the excentricity, as it determines the shape of the curve.

To ascertain the numerals of a series generally requires repeated trials. If z turns out negative, of course the numerals are wrongly chosen, but even in the case of its acquiring a positive value, the final test applied consists in working out the values and to select the numerals, that accord best with the experimental values. I have thus been forced to change the numerals, as given by Kaiser and Runge, in many instances.

A second difficulty is offered by the degree of exactness of the experimental values. The latter have been supplied by Kaiser and Runge, Liveing and Dewar, Lecoq de Boisbeaudran and Snow, and they do not always accord well. But even the values of one observer may greatly differ in exactness and may cause considerable discrepancies, which will show themselves most markedly in the red and ultrared rays.

Only a few lines do not seem to fit into any series. These lines are all of a slight intensity, they differ sometimes in aspect from the other lines or are omitted by other observers. I therefore conclude them to be due to impurities.

Several series of the same metal may be united either by the same root or the same excentricity or by both combined. In the Table of Wave Lengths I have bracketed those values.

The spectrum lines of each alkali metal seem to form two groups, divided by a large gap or interval, and appear to form two octaves, differentiated by their amplitudes especially. These gaps proceed towards the red with increasing atomic weight.

During the progress of my work I have been assisted by Mr. R. L. J. Ellery, late Director of the Melbourne Observatory, who aided me in solving difficult algebraical questions, and by Mr. W. Sutherland, the author of important works on molecular physics. To these gentlemen I hereby offer my grateful acknowledgment.

Lithium. The three equations, expressing the 3 series, are:

1. $3497 + \frac{15021}{n^2 - 5{\cdot}885} = \lambda^n$

2. $3497 + \frac{13428}{n^2 - 3{\cdot}85} = \lambda^n$

3. $2297 + \frac{5939}{n^2 - 2{\cdot}6535} = \lambda^n$

The line 3838 does not agree closely, but fits exactly into a Balmer formula, viz., $\lambda^n = 3731 \times \frac{n^2}{n^2 - 4}$, the head-line of which is 6708. The series, however, is not continuous.

Sodium is represented by 6 equations, viz.:

1. $4073{\cdot}5 + \frac{20125}{n^2 - 6{\cdot}36} = \lambda^n$

2. $4072 + \frac{20057}{n^2 - 6{\cdot}36} = \lambda^n$

3. $4085 + \frac{18387}{n^2 - 4{\cdot}532} = \lambda^n$

4. $4082{\cdot}5 + \frac{18343}{n^2 - 4{\cdot}532} = \lambda^n$

5. $2416{\cdot}7 + \frac{5946}{n^2 - 2{\cdot}201} = \lambda^n$

6. $2416{\cdot}7 + \frac{5935}{n^2 - 2{\cdot}201} = \lambda^n$

The two lines 5676 and 5670 are omitted as most likely belonging to a foreign metal, perhaps Titanium.

Potassium likewise furnishes 6 equations:

1. $4573{\cdot}5 + \frac{18865}{n^2 - 1{\cdot}022} = \lambda^n$

2. $4562 + \frac{18742}{n^2 - 1{\cdot}022} = \lambda^n$

3. $4578 + \frac{18170}{n^2 - 1{\cdot}153} = \lambda^n$

4. $4566 + \frac{18062}{n^2 - 1{\cdot}153} = \lambda^n$

5. $2860 + \frac{8151}{n^2 - 2{\cdot}133} = \lambda^n$

6. $2860 + \frac{8133}{n^2 - 2{\cdot}133} = \lambda^n$

TABLE OF WAVE LENGTHS OF THE ALKALIES.

–	LITHIUM.				SODIUM.						POTASSIUM.						RUBIDIUM.				CAESIUM.			
A.	1 & 2.	B.	3.	B.	1 & 2.	B.	3 & 4.	B	5 & 6.	B.	1 & 2.	B.	3 & 4.	B.	5 & 6.	B.	1 & 2.	B.	3 & 4.	B.	1 & 2.	B.	3 & 4.	B.
2			6708	6708					5896 5890	5896 5890	10908 10855	11550 10860	10927 10877	12200 11550	7226 7215	7699? 7666?	14162 13876	14750 13180	7562 7401	8450?	26317 24923		8341 7945	8330
3	8323 6104	8110 6104	3233	3233	11696 11669	11320	8200 8188	8200 8188	3303 3301	3303 3302	6936 6909	6939 6911	6893 6868	6911?	4047 4044	4047 4044	7729 7602	7950 7811	4216 4202	4216 4202	9099 8743	9000 8820	4593 4555	4593 4555
4	4972 4602	4972 4602	2741	2741	6161 6155	6161 6155	5689 5683	5688 5683	2853	2853	5832 5812	5832 5813	5802 5783	5802 5783	3447 3446	3447 3446	6299 6207	6299 6207	3592 3587	3592 3587	6974 6724	6974 6724	3889 3877	3889 3877
5	4273 4132	4273 4132	2562	2563	5153 5148	5154 5149	4984 4979	4984 4979	2679	2680	5360 5343	5360 5343	5340 5323	5340 5324	3217 3215	3218 3217	5725 5647	5724 5648	3351 3349	3351 3349	6214 6010	6213 6011	3617 3612	3617 3612
6	3986 3914	3986 3915	2475	2475	4752 4749	4752 4748	4669 4666	4669 4665	2593	2594	5113 5098	5113 5098	5100 5084	5100 5084	3101 3100	3102 3102	5433 5362	5432 5363			5843 5663	5845 5664		
7	3845 3794	3838 3795	2425	2426	4545 4542	4546 4543	4499 4494	4500 4494	2544	2544	4967 4952	4965 4952	4957 4943	4957 4943	3034 3033	3535	5263 5196	5260 5195			5637 5468	5635 5466		
8	„ 3720	3719	2394	2395	4422 4420	4424 4420	4394 4391	4394 4391	2514	2512	4874 4859	4871 4857	4867 4853	4864 4851	2992 2991	2992	5155 5091	5162 5086			5506 5345	5502 5346		
9	„ 3671	3671	2373	2374	4343 4341	4344 ?	4325 4323	4326 ?			4810 4796	4809 4797	4805 4792	4804 4789	2963	2963	5082 5020	5086 5022			5419 5262	5411 5258		
10			2357	2359							4764 4751	4760			2943	2943					5357 „	5346?		
11																					5313 „	5311		

Column A contains the serial number. Columns B, B the experimental wave lengths. Columns 1, 2, 3, 4, 3, 5, 6 the calculated values.